concentrations were found to vary spatially. Also, the wintertime sulfate pattern was likely to be more heterogeneous in space and time. This variation generally was independent of wind direction, but was related to local factors, such as the NH_3 concentration, population density, and distance from the center of the city.

### 6.5.1.6   Whiteface Mountain, New York

The AIRS sampling location at the Whiteface Mountain in Upstate New York is a high mountain top site elevated from the surrounding terrain. The monitoring site offers the possibility of comparing mountain top concentrations to the surrounding lower elevation sites. The seasonal pattern of PM_{10} concentration for Whiteface Mountain and the surrounding low elevation sites, Saranac Lake and Saratoga Springs, is shown in Figure 6-65. The concentration at the three sites is virtually identical during June through September. However, during the winter the mountain top site at Whiteface has a PM_{10} concentration which is only one third of the low elevation sites. This indicates that during the winter, the Whiteface mountain top is above the surface-based aerosol layer, while during the summer the height of the well mixed aerosol layer rises above the mountain top producing a reasonably uniform concentration at all sites.

6.5.2   Subregional Aerosol Pattern in the Southeast

6.5.2.1   Atlantic Coast States

The average yearly concentration in the southeast Atlantic coast states for all sites and trend sites has decreased from 32 to 24 μg/m^3 and 25 μg/m^3 (Figure 6-66a,b). The reductions were 25% and 22%. Seasonal concentrations show a summer peak largely due to $PM_{2.5}$ (Figure 6-66c). Comparison of three AIRS PM_{10} monitoring sites in North Carolina's Piedmont, Winston-Salem, Greensboro, and Raleigh-Durham (Figure 6-66d) shows virtually identical concentrations (within 10%), both in absolute magnitudes and in the seasonality with summer peaks in PM_{10}. This is an indication that these sites in this subregion are exposed to essentially the same air masses throughout the year. It also suggests that the excess PM_{10} concentrations due to local urban sources probably are not signficant.
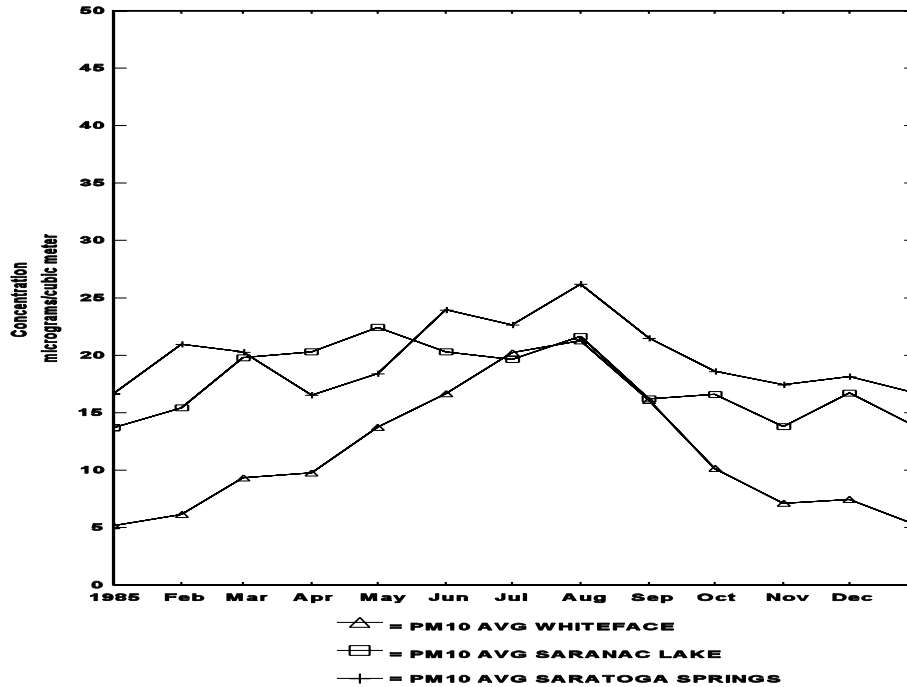
Figure 6-65. PM$_{10}$ concentration seasonality at Whiteface Mountain and neighboring low-elevation sites.

Size segregated monitoring data for Winston-Salem (Figure 6-66f) show that fine particles contribute 70 to 80% of the PM$_{10}$ mass of 25 to 35 μg/m^3. Coarse particles are seasonally invariant at about 10 μg/m^3 which is typical for eastern U.S.

The PM$_{10}$ concentration at monitoring sites in Florida (Orlando, Miami, Tampa) show virtually identical concentrations ranging between 25 to 30 μg/m^3 throughout the year, without appreciable seasonality (Figure 6-66e).

6.5.2.2   Texas and Gulf States

The average yearly concentration between 1988 and 1994 in the Texas-Gulf states has decreased for all sites and tend sites from 28 to 25 μg/m^3 (Figure 6-67b), a reduction of 11%. Seasonal concentrations show a summer peak largely due to PM2.5 (Figure 6-68c). The seasonal PM$_{10}$ concentration at sites in Odessa, Amarillo, and Lubbock, TX, and in New Orleans, LA, Mobile and Birmingham, AL show uniformity (20 to 40 μg/m^3) with modest seasonality
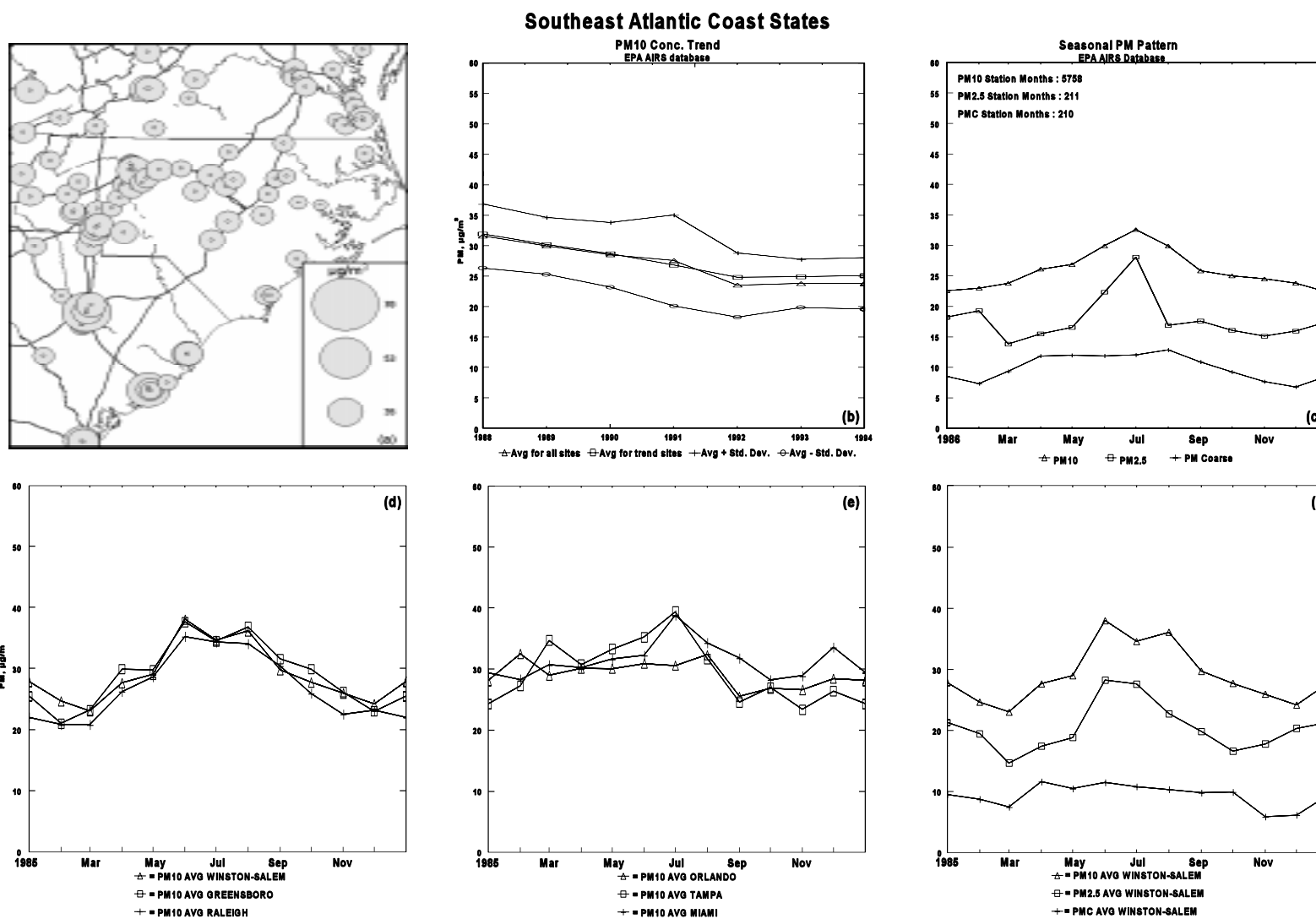
Figure 6-66. Aerosol concentration patterns for the Southeast Atlantic Coast states and sites in North Carolina and Florida: (a) monitoring sites, (b) trends, (c) seasonal pattern, (d) North Carolina sites, (e) Florida sites, and (f) seasonal pattern for Winston-Salem.
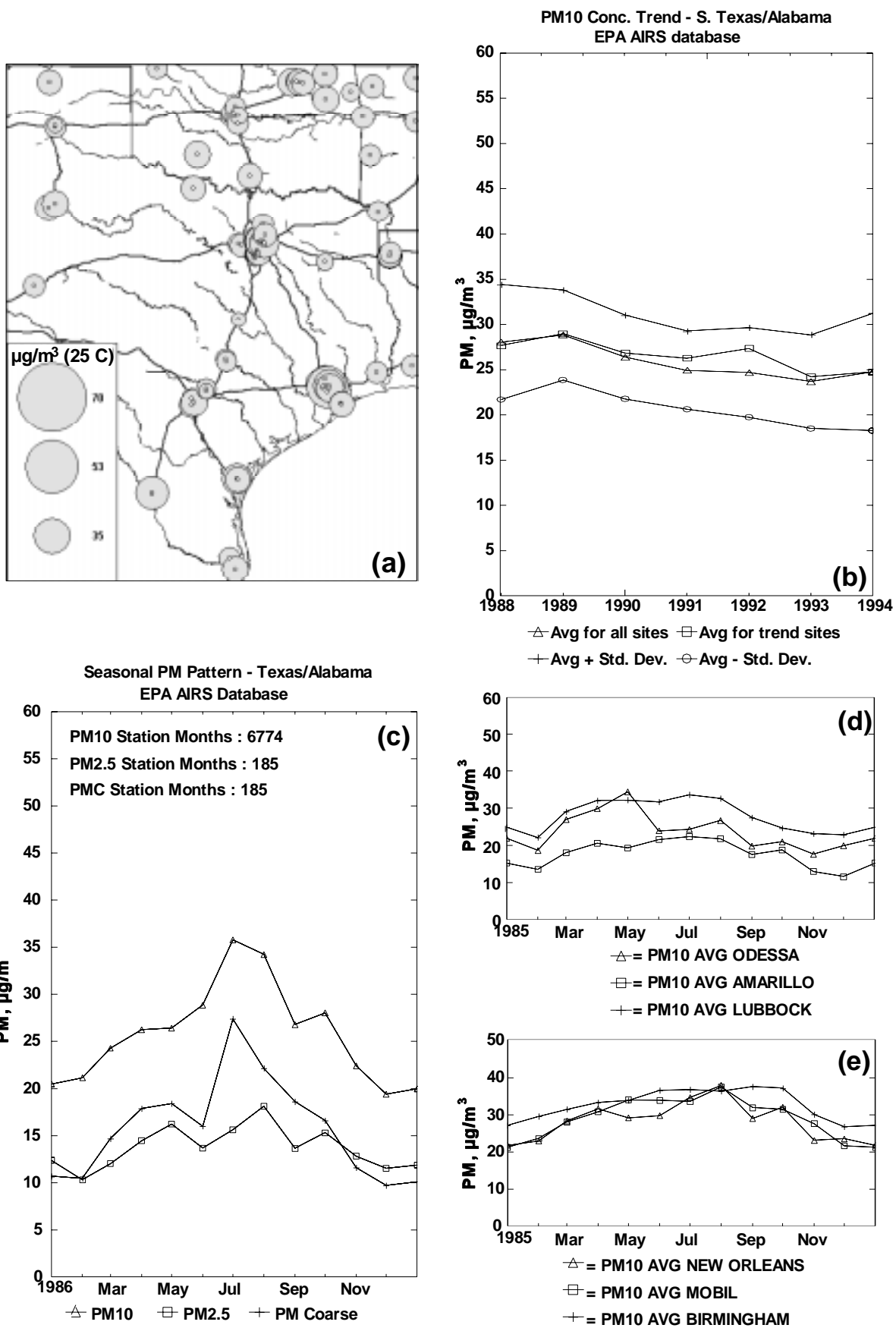
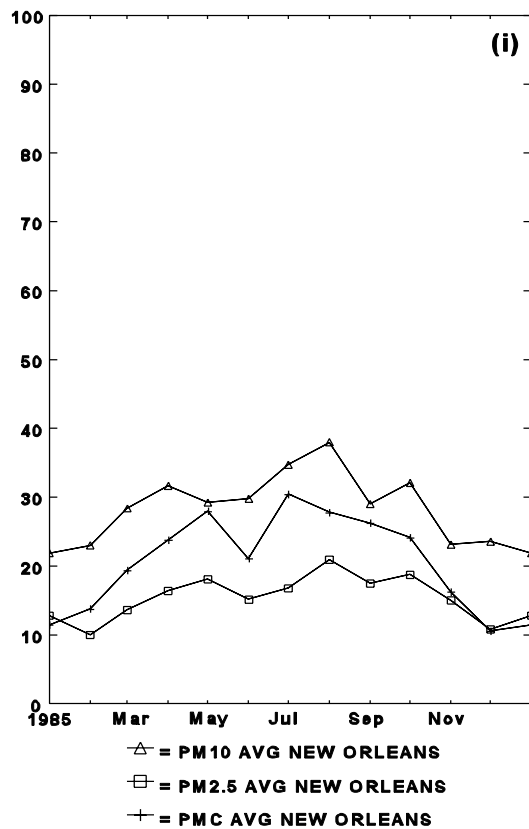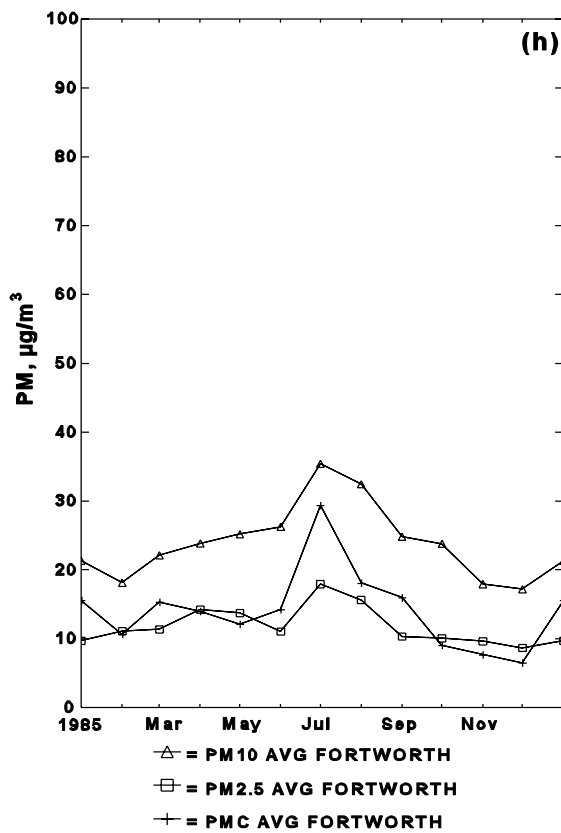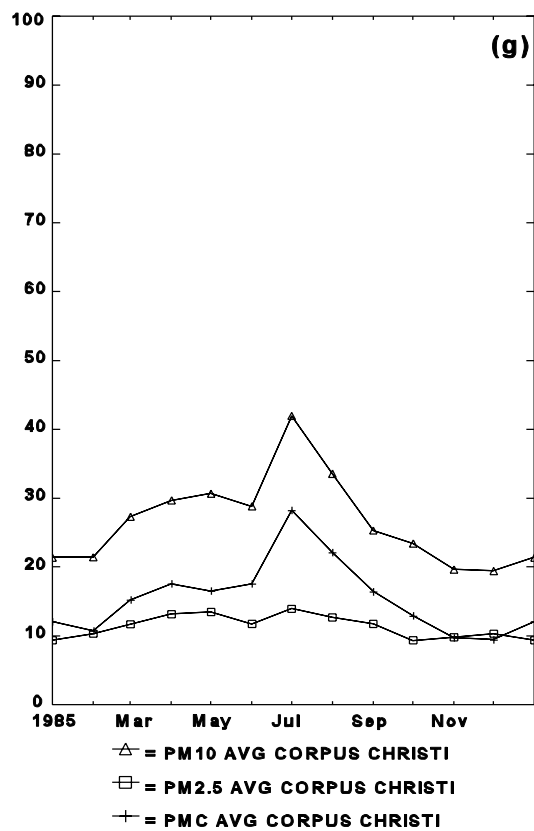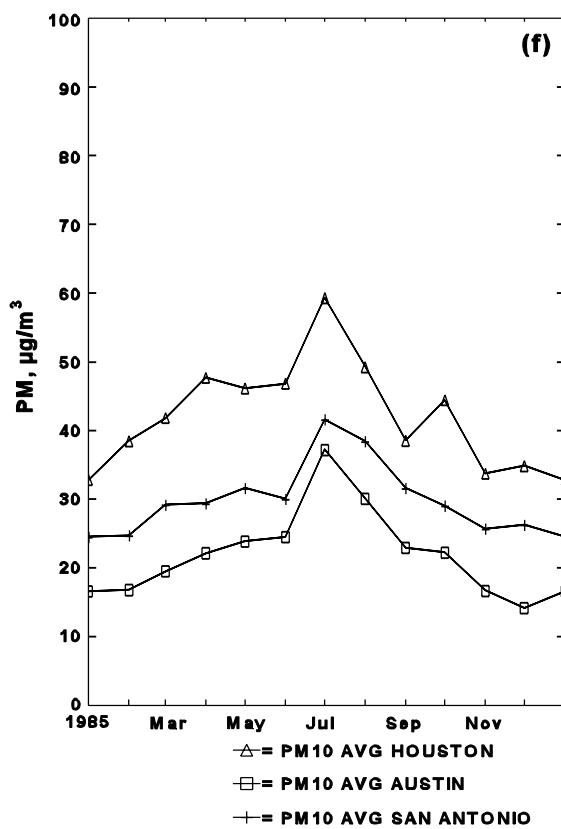**Figure 6-67a,b,c,d,e,f,g,h,i. Aerosol concentration patterns in Texas and Gulf states.**

Figure 6-67 (cont'd). Aerosol concentration patterns in Texas and Gulf states.

(Figure 6-67d,e). The sites in Houston, Austin, and San Antonio, TX show a wider range of PM_{10} values with summer peaks (Figure 6-67f).

The size segregated aerosol samples collected in the cities of the Gulf states, Corpus Christi, Forth Worth and New Orleans, LA (Figure 6-67g,h,i) all show fine particle concentrations that are relatively low (10 to 20 $\mu g/m^3$) compared to large eastern cities. Coarse particle concentrations, on the other hand, can account for more than half of the PM_{10} mass. The coarse particle contribution is most pronounced during the summer season.

In Houston, TX, Dzubay et al. (1982) found that in summertime fine particle mass contained 58% sulfate and 18% of carbonaceous material. They also found that the coarse fraction (2.5 to 15 μm) consisted of 69% crustal matter, 12% carbon, and 7% nitrate species.

6.5.2.3   Atlanta

Characterization of the Atlanta area aerosol (Marshall et al., 1986) show that elemental carbon and particulate sulfur represent, respectively 3.1 to 9.9% and 1.9 to 9.4% of the total suspended particulate mass. The concentrations of elemental carbon, sulfur, and TSP exhibit strong seasonal variations, with elemental carbon decreasing from winter to summer, and sulfur and TSP increasing. Elemental carbon appears to be statistically separate from sulfur, indicating that the sources for elemental carbon and particulate sulfur are distinct.

6.5.2.4   Great Smoky Mountains

Size segregated fine and coarse aerosol concentrations were measured at the Great Smoky Mountains National Park in September of 1980 (Stevens et al., 1980). Sulfate and its associated ions contributed to 61% of the fine particle mass, followed by organics (10%) and elemental carbon (5%).

6.5.3   Subregional Aerosol Pattern in the Industrial Midwest

Since the turn of the century, the major cities in the industrial midwestern states had air pollution problems due to smoke and dust. Pittsburgh, St. Louis, Chicago, and Detroit were among the formerly notorious air pollution hot spots. The recently acquired PM_{10} database now allows the re-examination of these metropolitan areas in the industrial Midwest for their concentration pattern in the 1990s.

6.5.3.1   Pittsburgh, Pennsylvania

The average PM_{10} concentrations for sites in the extended metropolitan area is shown in Figure 6-68. The Pittsburg, PA subregion includes the industrial cities, Steubenville, OH, and Weirton, OH, located on the Ohio River. The average PM_{10} concentration at the 80 sites shown on the map varies only by about 20% from site to site. Outstanding high concentration hot spots are now absent. It is thus evident that during the 1985 to 1993 period, the average PM_{10} concentrations in the Pittsburgh subregion were spatially rather uniform.

In the Pittsburgh, PA metropolitan area there was a decrease in the annual average PM_{10} concentrations between 1988 and 1994 from 37 μg/m^3 to 32 μg/m^3 for all sites and from 41 μg/m^3 to 33 μg/m^3 for trend sites (Figure 6-68b). The reductions were 14% for all sites and 19% for trend sites.   Figure 6-68b also marks the concentration standard deviation among the monitoring sites for each year, which is about 15 to 20% and shrinking over time.

The seasonality of the PM_{10} pattern (Figure 6-68c) is dominated by a summer peak (45 μg/m^3), which is about 50% higher than the winter concentrations (30 μg/m^3). The sites in Pittsburgh, PA, Weirton, OH, and Steubenville, OH (Figure 6-69) show comparable seasonality and values that are slightly above the subregional average. Hence, the particles at these formerly highly polluted locations are now virtually identical to their subregional background.

Size segregated aerosol samples in Pittsburgh, PA and Steubenville, OH (Figure 6-69) show that fine particles contribute 70 to 80% of the PM_{10} mass, and also dictate the summer-peak seasonality of the PM_{10} concentrations. As in other urban monitoring sites in the eastern U.S., the coarse particle concentration in Pittsburgh is about 10 μg/m^3 and seasonally invariant. The size segregated seasonal data for Steubenville, OH, exhibit more random fluctuations as well as a discrepancy between the sum of fine and coarse on one hand, and PM_{10} on the other. The discrepancy is attributed to the small number of size segregated aerosol samples.

Sulfate acidity measurements (Waldman et al., 1991) at Chestnut Ridge, PA (east of Pittsburgh), suggest higher acidity occurred in the overnight period (0000-0800) in the late fall, while sulfate had its highest levels in the morning to afternoon period.
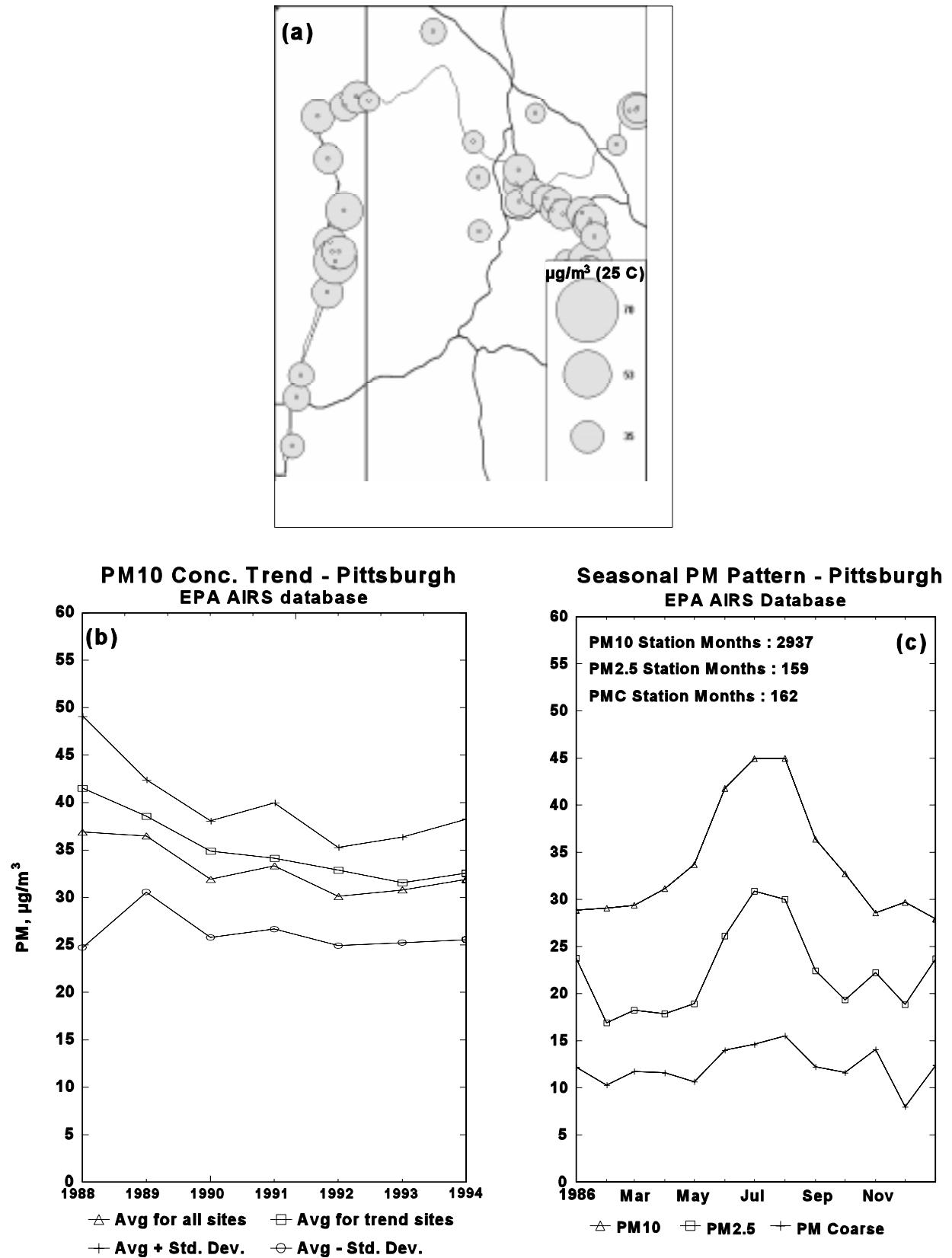
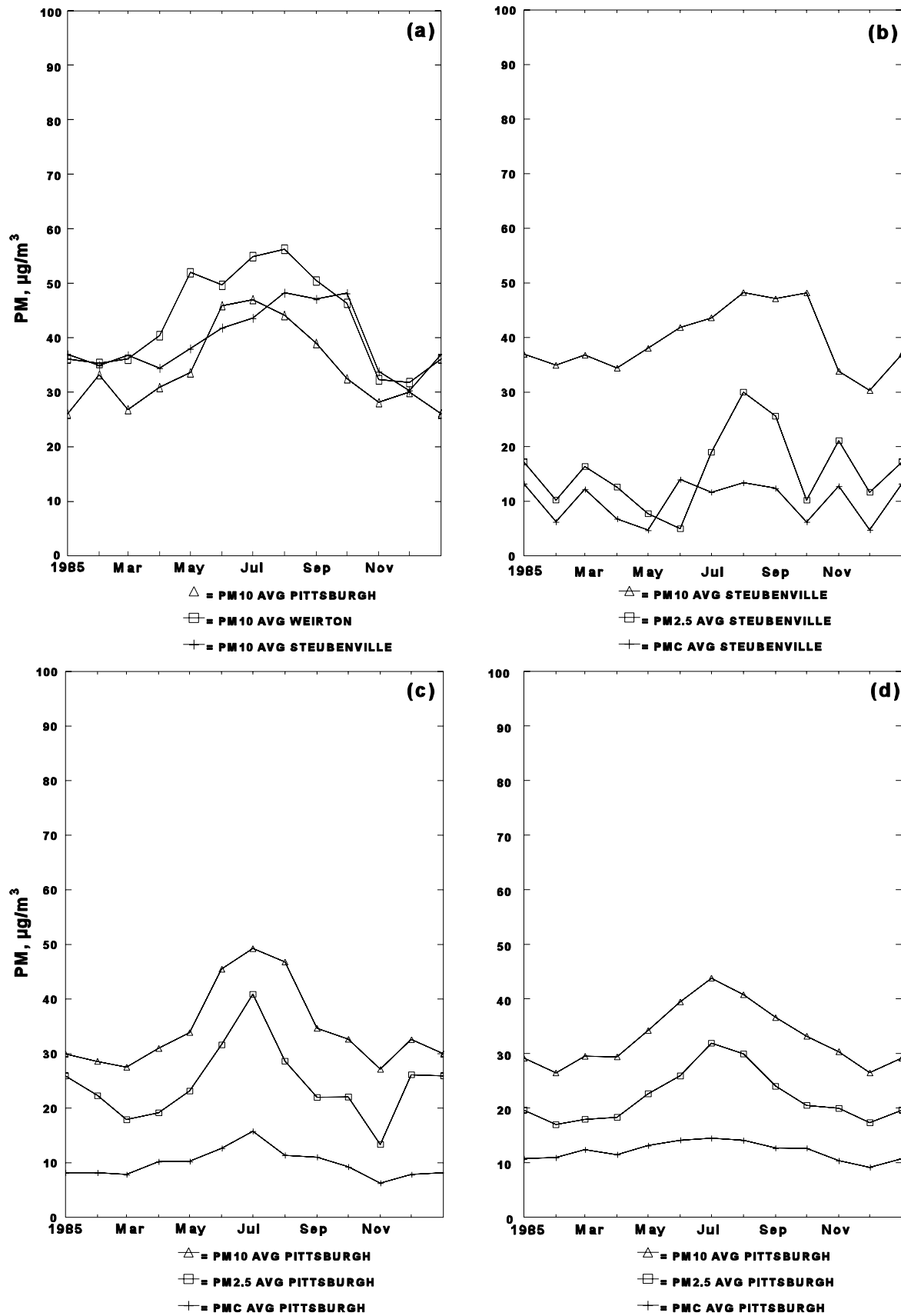**Figure 6-68.** Pittsburgh subregion: (a) aerosol concentration map, (b) trends, and (c) seasonal pattern.

Figure 6-69a,b,c,d.   Fine, coarse, and PM$_{10}$ concentration at sites in or near Pittsburgh.

Pierson et al. (1980b, 1989) found no appreciable night/day difference in aerosol H^+ (or NH_4^+ or SO_4^{2-}) - and almost no diurnal variation in O_3 - at two elevated sites (Allegheny Mountain and Laurel Hill, elevations 838 and 850 m) in southwest Pennsylvania. The contrast with behavior at lower sites and particularly with the concurrent measurements at Deep Creek Lake (Vossler et al., 1989) is attributable to isolation from ground-based processes at the elevated sites at night.

The remarkable uniformity of fine particle mass and elemental composition from site to site in the Ohio River Valley was also shown by Shaw and Paur (1983). Sulfur was the predominant element in fine particles. Factor analysis of element concentrations indicated three clusters throughout the year (1) coarse particle crustal elements (2) fine particle sulfur and selenium (3) fine particle manganese, iron and zinc.

The chemical mass balance of Weirton-Steubenville aerosol was examined by Skidmore et al. (1992). Primary aerosols from motor vehicles and secondary ammonium sulfate were dominant contributors to the $PM_{2.5}$ aerosol. Steel emissions were also significant contributors to $PM_{2.5}$. Wood burning and oil combustion were occasionally detected. Geological material was the major contributor to the coarse aerosol fraction. Primary geological material, primary motor vehicle exhaust, and secondary sulfate were the major contributors to PM_{10} at all five monitoring sites.

The composition of size-fractionated summer aerosol in nearby Charleston, West Virginia was reported by Lewis and Macias (1980). Ammonium sulfate was the largest single chemical component (41%) of the fine aerosol mass. Carbon was also a large component of both fine and coarse particle mass constituting 16% and 12% respectively. Factor analysis indicated that four factors were sufficient to satisfactorily represent the variance of 26 measured parameters. The factors were characteristic of crustal material, ammonium sulfate, automotive emissions, and unidentified anthropogenic sources.

6.5.3.2   St. Louis, Missouri

Historically, the St. Louis metropolitan area has been known for high particulate concentrations. The map of the metropolitan area (Figure 6-70a) shows about factor of 2 to 3 concentration differences among the PM_{10} monitoring stations.
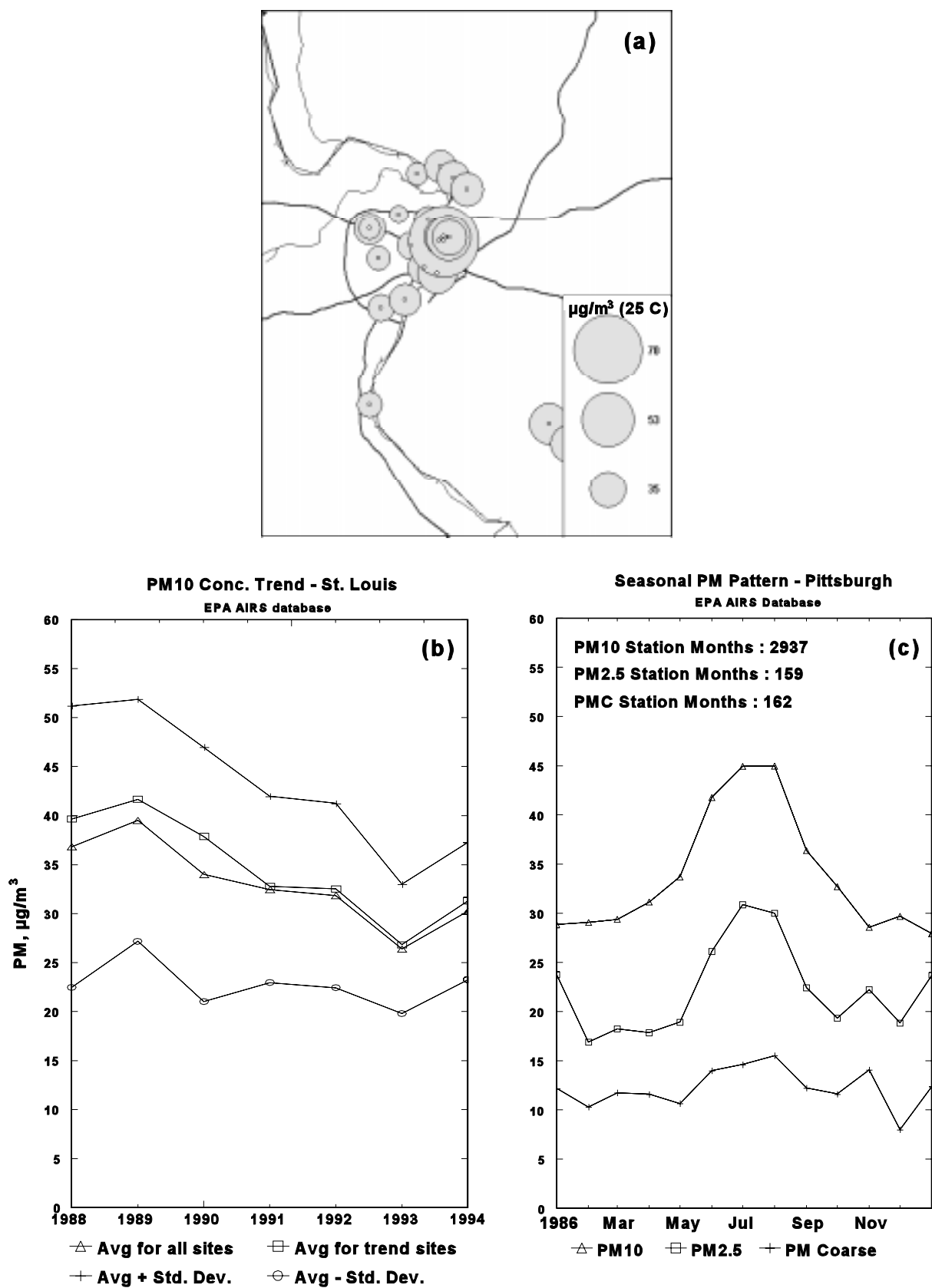
Figure 6-70. St. Louis subregion: (a) aerosol concentration map, (b) trends, and (c) seasonal pattern.

In the St. Louis metropolitan area there was a decrease in the annual average PM_{10} concentration between 1988 and 1994 from 37 $\mu g/m^3$ to 30 $\mu g/m^3$ for all sites and from 40 $\mu g/m^3$ to 31 $\mu g/m^3$ for trend sites (Figure 6-70b). The reductions were 23% for all sites and 22% for trend sites. This decline is comparable to the average reductions over the industrial midwestern region. The seasonality of the sub-regionally averaged concentrations (Figure 6-70c) shows the summer peak with 40 to 50 $\mu g/m^3$ which is about 50% higher than the winter averages.

Seasonal comparison of the individual monitoring sites in the area shows that Granite City, IL and East St. Louis, IL have higher PM_{10} concentrations throughout the year compared to western St. Louis, MO sites.

Size segregated aerosol samples at three sites west of the Mississippi River (Ferguson, MO, Affton, MO, and Clayton, MO) show that fine particles are mostly responsible for PM_{10}, including the seasonality (Figure 6-71). Coarse particles contribute 10 $\mu g/m^3$ or less throughout the year, although corresponding size segregated aerosol data for the more polluted east side of the Mississippi River are not available.

Monitoring the diurnal and seasonal patterns of particulate sulfur and sulfuric acid in St. Louis, Cobourn and Husar (1982) noted an afternoon increase in particulate sulfur concentration of about 20%. For the summertime, particulate sulfur concentration was higher than the annual mean by 40%.

Measurements were made using dichotomous samplers of PM_{10} (expressed as PM_{20}), $PM_{2.5}$ and S at urban, suburban, semi-rural, and rural sites in and around St. Louis, MO, during 1975 to 1976 as part of the Regional Air Pollution Study (RAPS) (Altshuller, 1982). Unlike the nonurban sites compared from the IMPROVE/NESCAUM network with urban sites from AIRS, these rural sites were within 45 km of the center of St. Louis. The comparisons are between three urban sites (103, 105, 106) and three rural sites (118, 112, 124).

The $PM_{2.5}$ constituted 45 to 60% of the PM_{10} with the percentages at rural sites ranging from 0 to 10% higher than at urban sites. The ratios of the concentrations of $PM_{2.5}$ at urban sites to $PM_{2.5}$ at rural sites ranged from 1.4 to 1.5 for the six quarters between the third quarter of 1975 to the fourth quarter of 1976. The ratios of the concentrations of PMCoarse at urban sites to PMCoarse at rural sites ranged from 1.5 to 1.8 for the same six quarters. For fine S, the ratios
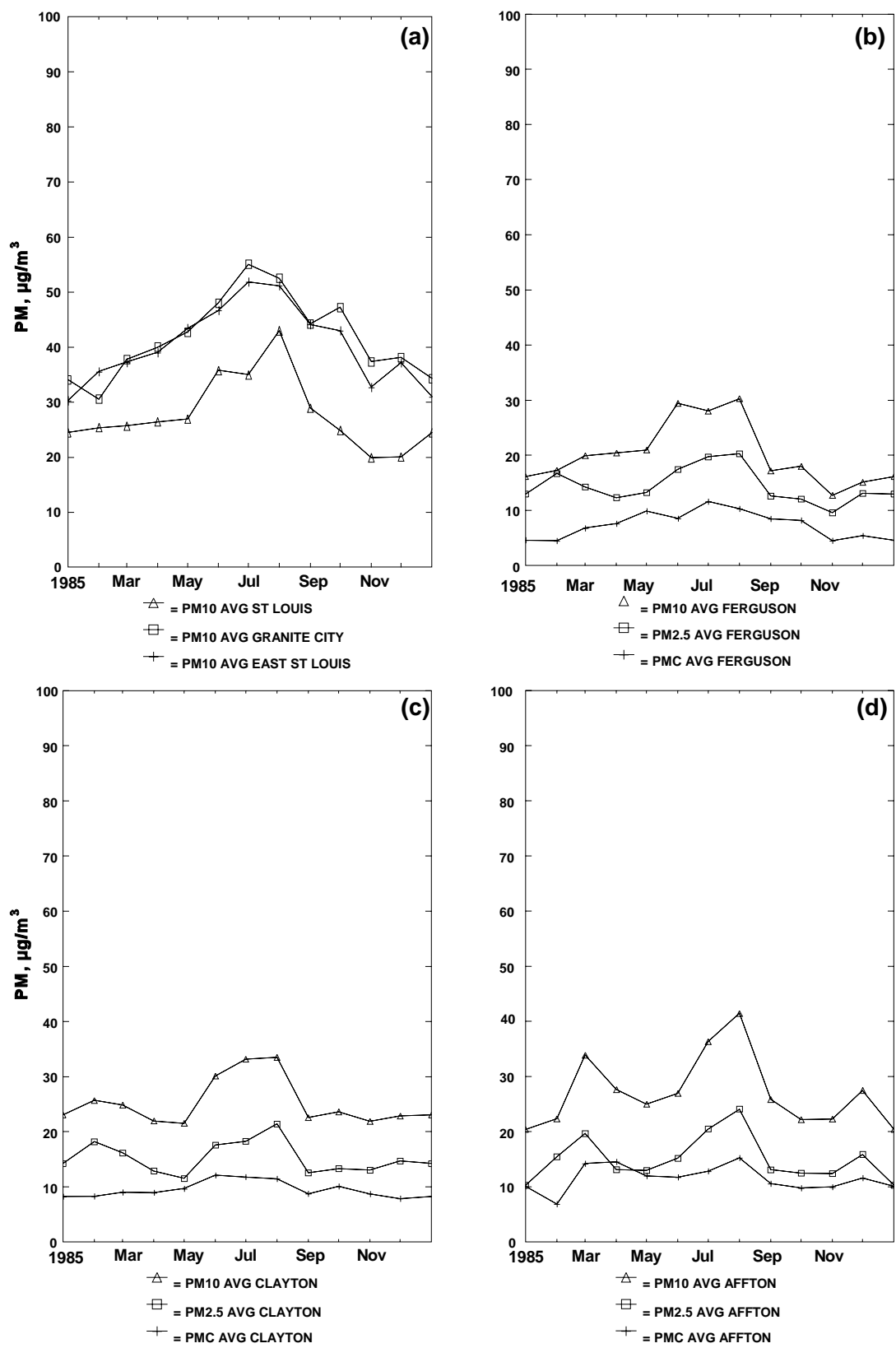
Figure 6-71a,b,c,d. Fine, coarse, and PM$_{10}$ seasonal concentration patterns in or near St. Louis.

between urban and rural sites ranged from 1.1 to 1.2, while for coarse S, the ratios between urban and rural sites ranged from 1.7 to 2.6 for the same six quarters.

These results indicate a very strong regional influence on fine S with a lesser regional influence on $PM_{2.5}$. The ratios of PMCoarse and coarse S indicate stronger local influences on their concentrations than on fine S and $PM_{2.5}$. The percentage of fine S expressed as $(NH_4)_2 SO_4$ to the $PM_{2.5}$ was consistently higher at rural sites than at urban sites in and around St. Louis (Altshuller, 1982). In the third quarters of 1975 and 1976, these percentages averaged 70% at rural sites and 55% at urban sites, while in the fourth quarters of 1975 and 1976, these percentages averaged 45% at rural sites and 35% at urban sites.

As observed near New York City (Leaderer et al., 1982), the fine S in the St. Louis area was regionally homogenous and, during episodic periods, the fine S concentrations followed the variations in O_3 concentrations reasonably closely (Altshuller, 1985). A linear relationship was obtained for fine S and O_3 flows into St. Louis. The fine S with increasing fine S concentration constituted an increasingly large percentage of the $PM_{2.5}$ at an urban site (Altshuller, 1985).

6.5.3.3 Chicago, Illinois

Historically, Chicago has been known for industrial dust, smoke, and haze, as in adjacent East Chicago and Gary, IN. The average PM_{10} concentrations over the Chicago subregion (Figure 6-72a) vary by a factor of two or less throughout the subregion. In the Chicago subregion, there was a decrease in the annual average PM_{10} concentrations between 1988 and 1994 from 32 $\mu g/m^3$ to 29 $\mu g/m^3$ for all sites and from 39 $\mu g/m^3$ to 31 $\mu g/m^3$ for trend sites (Figure 72b). The reductions were 9% for all sites and 20% for trend sites. The seasonality of PM_{10} is also typical with the summer peak of 40 $\mu g/m^3$ and winter values of 20 to 30 $\mu g/m^3$.

Superposition of seasonal PM_{10} data at Chicago, IL, East Chicago, IL, and Gary, IN, demonstrates significant spatial uniformity, as well as indicating in more recent years comparatively low PM_{10} concentrations in this area that has historically been a smoky and dusty industrial subregion.

In the Chicago subregion there was a decrease in the annual average PM_{10} concentration between 1985 and 1994 from 40 $\mu g/m^3$ to 29 $\mu g/m^3$ for all sites and from 40 $\mu g/m^3$ to 31 $\mu g/m^3$ for trend sites (Figure 6-72b). The reductions were 28% for all sites and 23% for trend sites.
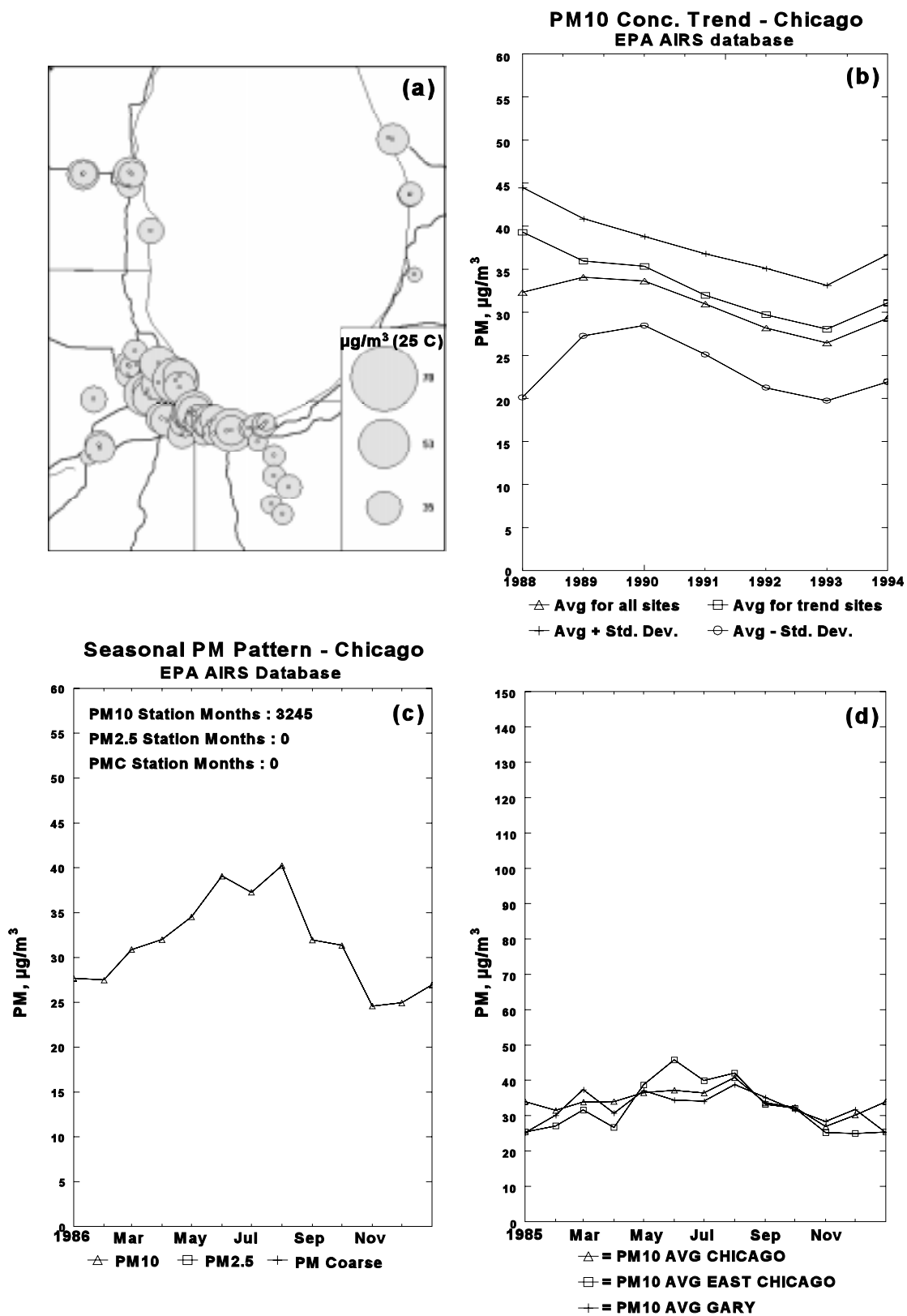
Figure 6-72. Chicago subregion: (a) aerosol concentration map, (b) trends, (c) and (d) seasonal patterns.

Chemical composition measurements in Chicago (Lee et al., 1993) showed that mean concentrations for SO_4^{2-} (5.55 $\mu g/m^3$), NH_4^+ (2.74 $\mu g/m^3$), NH_3 (1.63 $\mu g/m^3$), HNO_3 (0.81 $\mu g/m^3$), HNO_2 (0.99 $\mu g/m^3$), for SO_2 (21.2 $\mu g/m^3$), NO_3^- (4.21 $\mu g/m^3$), and H^+ (7.7 $nmol/m^3$). The highest values occurred in the summer, except for HNO_2 and NO_3^- which had the highest values in the winter.

Comparison of atmospheric coarse particles at an urban and nonurban site near Chicago, IL, show that the concentration were 50% higher during mid-day than at night. Dry ground samples were 30 % higher than wet ground and 90% higher than frozen ground samples. (Noll et al., 1985).

The analysis of coarse particles in Chicago, IL (Noll et al., 1990) show that the coarse particle mass could be divided into two categories: material that was primarily of crustal origin (Al, Ca, Fe, and Si) and material that was primarily of anthropogenic origin (Cd, Cu, Mn, Ni, Pb, and Zn). The mass of crustal material varied between 14 and 24% of the total coarse mass. The mass of Cd, Cu, Mn, Ni, Pb, and Zn totaled less than 1%.

The composition of atmospheric coarse particles at urban (Chicago, IL) and nonurban (Argonne, IL) were reported by Noll et al. (1987). Limestone and silicates were the main source of material at the non urban site. Anthropogenic sources, represented by flyash and coal, were present in the industrial sector sample and rubber tire was present in the commercial sector sample.

6.5.3.4   Detroit, Michigan

In Detroit, in July, 1981 (Wolff and Korsog, 1985) the average fine mass was found to be 42.4 $\mu g/m^3$. The chemical composition of the fine particles (Wolff et al., 1982) was 52% sulfates, 27% organic carbon, 4% elemental carbon, 8% soil dust. Nitrate was found to be absent from fine mass. Fine particles themselves contributed about 64% of the aerosol mass. The sulfate associated with coal combustion contributed to 50% of the fine particles. The coarse fraction, which averaged as 25.8 $\mu g/m^3$, was dominated by crustal material which accounted for about two-thirds of the coarse material. Significant contributions were also identified from motor vehicles (mostly due to re-entrained road dust) and iron and steel industry emissions.